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**Title of the Invention: Polarizable Electrode Body and Method for
Manufacturing Same**

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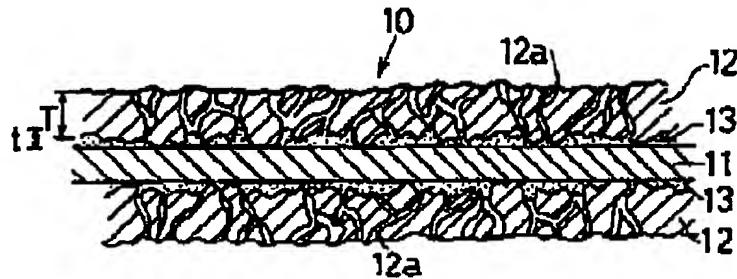
(54) [Title of the Invention] Polarizable Electrode Body and Method for Manufacturing Same

(57) [Summary]

[Object] To provide a polarizable electrode that improves the joining strength and state of contact between a collector and electrode material in an electrode body, is readily suited to continuous manufacture, and has a high electrical capacity and low internal resistance; a method

for manufacturing same; and an electric double-layer capacitor in which the polarizable electrode is used.

[Means of Achievement] In a polarizable electrode body wherein both sides of a collector are laminated with a porous electrode sheet composed mainly of active carbon, the collector and electrode sheet are laminated with a conductive adhesive layer containing conductive carbon and a binder interposed therebetween, and some of the conductive adhesive layer penetrates into holes of the electrode sheet, with the degree of penetration thereof being 0.15 to 30% of the thickness of the electrode sheet.



[Claims]

[Claim 1] A polarizable electrode body wherein both sides of a collector are laminated with a porous electrode sheet composed mainly of active carbon;

 said polarizable electrode characterized in that said collector and said electrode sheet are laminated with a conductive adhesive layer containing conductive carbon and a binder interposed therebetween; and

 some of the conductive adhesive layer penetrates into holes of said electrode sheet, with the degree of penetration thereof being 0.15 to 30% of the thickness of said electrode sheet.

[Claim 2] The polarizable electrode body as defined in Claim 1 wherein the largest pore diameter in said electrode sheet is 0.5 to 2.0 μm .

[Claim 3] The polarizable electrode body as defined in Claim 1 or 2 wherein the porosity of said electrode sheet is 40 to 90%.

[Claim 4] The polarizable electrode body as defined in any of Claims 1 through 3 wherein said collector is at least one metal selected from among aluminum, stainless steel, titanium, and tantalum that is fashioned into the form of a foil, plate, or sheet.

[Claim 5] The polarizable electrode body as defined in any of Claims 1 through 4 wherein said collector is composed of metallic foil, a thin metallic plate, or a metallic sheet whose surface has irregularities; and

 some of said conductive adhesive layer formed between said collector and said electrode sheet has penetrated into concave portions of said collector.

[Claim 6] The polarizable electrode body as defined in Claim 5 wherein some convex portions of said collector are in contact with said electrode sheet.

[Claim 7] The polarizable electrode body as defined in Claim 5 or 6 wherein said collector is metallic foil, a thin metallic plate, or a metallic sheet whose surface has been etched rough.

[Claim 8] The polarizable electrode body as defined in Claims 1 through 7 wherein said conductive carbon is graphite or carbon black.

[Claim 9] The polarizable electrode body as defined in any of Claims 1 through 8 wherein the average particle diameter of said conductive carbon is 0.5 to 50 μm .

[Claim 10] The polarizable electrode body as defined in any of Claims 1 through 9 wherein said binder is at least one type selected from among plasticized resins, cellulose derivatives, and water glass.

[Claim 11] An electric double-layer capacitor characterized in that a plurality of the polarizable electrode bodies defined in Claims 1 through 10 are provided in proximity in a row arrangement, a separator is provided between adjoining polarizable electrode bodies, and regions between said polarizable electrode bodies and said separator are filled with an electrolyte.

[Claim 12] A method for manufacturing a polarizable electrode body, characterized in comprising the steps of:

applying a conductive adhesive liquid comprising a conductive adhesive dispersed in a dispersant on a surface of an electrode sheet and/or a collector;

layering said electrode sheet and said collector with said applied conductive adhesive liquid interposed therebetween; and

removing said dispersant from said conductive adhesive liquid that is present in the region between the layered electrode sheet and collector.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a polarizable electrode body having exceptional adhesive strength between the electrode sheet and collector, while having low internal resistance; a method for manufacturing same; and an electric double-layer capacitor in which the polarizable electrode body is used.

[0002]

[Prior Art] Types of conventional electric double-layer capacitors include coin or button types, in which a separator is interposed between a pair of polarizable electrodes, with the resulting assembly being sealed along with an electrolyte using a metallic case, a sealing plate, and a gasket that insulates the two from each other; coil types, in which long electrode sheets and separators are layered together and coiled to produce an electric double layer capacitor unit that is then housed in a metal case, impregnated with an electrolyte, and sealed; and stacked types, in which a rectangular electrode thin film and a separator are laid over each other in an alternating fashion to produce an electrode laminate, and the positive and negative electrode leads of the electrode are each crimped and thereby connected, respectively, to the positive and negative electrode leads to produce an electric double-layer capacitor unit that is then housed in a metal case, impregnated with an electrolyte, and sealed.

[0003] Electric double-layer capacitors used in power applications for electric automobiles or the like must possess high energy densities and high output densities so as to achieve high unit volume capacitance and low internal resistance. In order to meet these requirements, investigations have been conducted into making the electrode body into a thin film and increasing the surface area of the electrode body to thereby increase the opposing area of the electrode body. It shall be apparent that the electric double-layer capacitor must also be exceptionally well-suited to mass production.

[0004] To increase the opposing area of the electrode body and make the electrode body into a thin film, an electrode body in the form of a sheet or thin film is produced by ① a method in which a mixture in the form of a paste or ink containing the electrode material is applied on or otherwise affixed to a collector, dried (solvent removal), and subsequently rolled or otherwise worked; or ② a method in which an electrode sheet comprising an electrode material is prepared in advance, a collector is laid atop the surface of the resulting electrode sheet, and the two are then rolled with rollers or otherwise formed into an integrated unit.

[0005] In order to reduce internal resistance in the electric double-layer capacitor in such manufacturing methods, it is important to improve contact-integration between the electrode material and the collector. Active carbon, acetylene black, and other carbon-based powder granules with good conductivity are thus generally used as the electrode material. As shown in FIG. 7, the electrode material layer or electrode sheet (subsequently referred to as "electrode material layer 2" when no distinction is made between the two) composed of carbon-based granules is a porous layer in which the spaces between the granules are holes 3 and whose surface is irregular. For this reason, if a metallic foil, metallic sheet, or another smooth-surfaced material is used as the collector 1, the interface between the collector 1 and the electrode material layer 2 contacts only in points, and the actual contact area thus decreases. This causes not only a decrease in the joining strength between the collector 1 and the electrode material layer 2, but also an increase in electric resistance due to the increase in the air portion (or liquid-phase portion when filled with electrolyte) 4 interposed between the collector 1 and the electrode material layer 2, thus causing the characteristics of the electric double-layer capacitor to deteriorate.

[0006] An electrode in which a collector having an irregular surface is used has been proposed in order to maintain the contact area between the collector and the electrode material layer.

[0007] Examples of proposed electrode bodies that have been produced using method ① include an electrode body wherein an aluminum net is used as a collector, and an electrode material composed of activated carbon powder is dispersed and admixed with a fluoropolymer-methyl alcohol mixture to yield a paste, which is then applied to the aluminum net (JP (Kokai) 4-162510); an electrode body wherein acetylene black and activated carbon powder, used as an electrode material, are admixed with a mixed solution of water and methanol, and an aqueous solution of carboxymethyl cellulose is added to the resulting solution to form a slurry, which is then applied to a collector composed of a surface-roughened aluminum foil (JP (Kokai) 4-162510); and an electrode body wherein polyvinyl pyrrolidone and an aqueous dispersion of polytetrafluoroethylene are added as a binder to an electrode material composed of activated carbon powder and acetylene black, and the resulting mixture is then applied to a collector composed of aluminum expanded metal (U.S. Pat. No. 4,327,400). An example of proposed electrode bodies that have been produced using method ② include a thin-profile electrode body wherein activated carbon and a conductivity-imparting agent are bonded using polytetrafluoroethylene as a binder to yield an electrode material sheet, the resulting sheet is superposed on a collector consisting of a metallic foil whose surface has been etched rough and a metallic plate having openings such as with an expanded metal, and the resulting assembly is then rolled with rollers to increase the joining integrity (JP (Kokoku) 54-12620).

[0008]

[Problems to Be Solved by the Invention] However, as mentioned above, even with collectors composed of punched metal or expanded metal with openings or a metallic foil with surface irregularities, the contact area cannot be regarded as adequate, and further improvements in the joining strength between the electrode material layer and the collector are required for the collector to be able to adequately withstand the feed tension and winding tension encountered during continuous electrode production in which a roll configuration is employed. Furthermore, in order to achieve higher output densities, the internal resistance must be reduced further; i.e., the airspace between the electrode material layer and the collector must be reduced.

[0009] With collectors made of expanded metal or other materials having openings, enlarging the openings is believed to facilitate engagement between the irregularities on the surface of the electrode sheet and the openings of the collector. However, enlarging the openings in the

expanded metal or other material may reduce the strength of the collector, and, since the sectional area per unit of the collector decreases, it is possible that the power-collecting effect of the collector will be inadequate, and obstructions related to increasing the capacity per unit volume of the electric double-layer capacitor will be presented.

[0010] With the foregoing circumstances in view, it is an object of the present invention to provide a polarizable electrode that improves the joining strength and state of contact between a collector and electrode material in an electrode body, is readily suited to continuous manufacture, and has a high electrical capacity and low internal resistance; a method for manufacturing same; and an electric double-layer capacitor in which the polarizable electrode is used.

[0011]

[Means Used to Solve the Above-Mentioned Problems] The polarizable electrode body of the present invention is a polarizable electrode body wherein both sides of a collector are laminated with a porous electrode sheet composed mainly of active carbon, and is characterized in that the collector and electrode sheet are laminated with a conductive adhesive layer containing conductive carbon and a binder interposed therebetween; and some of the conductive adhesive layer penetrates into holes of the electrode sheet, with the degree of penetration thereof being 0.15 to 30% of the thickness of the electrode sheet.

[0012] The largest pore diameter in the abovementioned electrode sheet is preferably 0.5 to 20 μm , while the porosity is preferably 40 to 90%.

[0013] The collector is preferably at least one metal selected from among aluminum, stainless steel, titanium, and tantalum that is fashioned into the form of a foil, plate, or sheet.

[0014] The abovementioned collector is preferably composed of a metallic foil, a thin metallic plate, or a metallic sheet whose surface has irregularities; and some of the conductive adhesive layer formed between the collector and the electrode sheet has preferably penetrated into concave portions of the collection material. In addition, some convex portions of the collector are preferably in contact with the electrode sheet.

[0015] The collector is preferably composed of a metallic foil, a thin metallic plate, or a metallic sheet whose surface has been etched rough.

[0016] In the abovementioned conductive adhesive, the conductive carbon preferably is graphite or carbon black, the average particle diameter of the conductive carbon is preferably 0.5 to 50 μm , and the binder preferably is at least one type chosen from among plasticized resins, cellulose derivatives, and water glass.

[0017] The electric double-layer capacitor of the present invention is characterized in that a plurality of the polarizable electrode bodies of the present invention are provided in proximity in a row arrangement, a separator is provided between adjoining polarizable electrode bodies, and regions between the polarizable electrode bodies and the separator are filled with an electrolyte.

[0018] The method for manufacturing a polarizable electrode body of the present invention is characterized in having the steps of applying a conductive adhesive liquid consisting of a conductive adhesive dispersed in a dispersant on a surface of an electrode sheet and/or a collector; layering the electrode sheet and collector with the applied conductive adhesive liquid interposed therebetween; and removing the dispersant from the conductive adhesive liquid that is present in the region between the layered electrode sheet and collector.

[0019]

[**Embodiments of the Invention**] First, an embodiment of the polarizable electrode body of the present invention shall be described with reference to FIG. 1.

[0020] A polarizable electrode body 10 is characterized in that a porous electrode sheet 12,12 composed mainly of active carbon is laminated onto both sides of a collector 11 with a conductive adhesive layer 13,13 interposed therebetween, and in that a conductive adhesive constituting the conductive adhesive layer 13 penetrates through to hole regions 12a in the porous electrode sheet 12.

[0021] The electrode sheet 12 is obtained by admixing a suitable carbon black, polytetrafluoroethylene powder, or the like with a carbon electrode material composed of activated carbon; introducing ethanol, oil, or the like; and obtaining a porous sheet by using rolls to roll the resulting mixture or by using an alternative method. In other words, a porous sheet is formed in which the regions between the activated carbon granules are holes 12a. It must be noted that the term "sheet" as referred to in the present specification includes films.

[0022] Activated carbon conventionally used as a carbon electrode can be used as the activated carbon that is the raw material of the electrode sheet 12. Specific examples include wood coal,

coconut husk coal, brown coal, saw dust, and other non-carbonized materials activated by water vapor, carbon dioxide, or another gas; and materials activated by zinc chloride or another chemical agent. The activated carbon may be in a powdered or granular form. The specific surface area of the activated carbon is significantly enlarged through activation, thus allowing an electrode having a large electric capacity per unit volume to be formed.

[0023] The diameter of the largest pore (maximum pore diameter) in the electrode sheet 12 is preferably 0.5 to 20 μm . If the maximum pore diameter is less than 0.5 μm , the conductive adhesive will not readily penetrate the hole regions 12a of the electrode sheet 12. If the maximum pore diameter is greater than 20 μm , the conductive adhesive will penetrate deep within the holes 12a of the electrode sheet, and thus becomes difficult to maintain at the interface between the collector 11 and the electrode sheet 12, and, in addition, the fine pores within the activated carbon will be covered by the conductive adhesive, and the performance of the capacitor will inevitably decline. It must be noted that the maximum pore diameter, as referred to in the present specification, is measured in terms of the bubble point in ethanol according to ASTM-E-128-61.

[0024] The porosity of the electrode sheet 12 is preferably 40 to 90%, and is more preferably 60 to 80%. If the porosity is less than 40%, less of the conductive adhesive constituting the conductive adhesive layer 13 will be able to penetrate into the holes 12a of the electrode sheet 12, and accordingly, an adequate improvement in the joining strength cannot be realized even if the conductive adhesive layer 13 is used. On the other hand, if the porosity is greater than 90% and if an insufficient amount of conductive adhesive is used, some of the holes 12a will not be filled with the conductive adhesive, and the effect in terms of improving the joining strength will thus be inadequate. Furthermore, a layer of air (or, when a capacitor is formed, a liquid-phase region that is formed from the introduction of the electrolyte) forms in the region next to the collector 11, which causes the internal resistance to decrease. On the contrary, if the conductive adhesive is not introduced in an adequate amount, it will penetrate deep into the holes 12a of the electrode sheet 12 and most of the fine pores of the activated carbon constituting the electrode sheet 12 will thereby be covered, thus reducing the specific area of the activated carbon, which accompanies a decline in the performance of the capacitor. Porosity (expressed as a percentage), as referred to in the present specification, refers to the value determined to be the ratio of the hole volume (V_0) to the total volume (V) in all of the electrode sheets 12 ($(V_0/V) \times 100$). The

hole volume was obtained using the formula below, wherein the volume of the consolidated region of the electrode sheets 12 (W/ρ), which is obtained from the real density of the electrode sheets 12 (ρ) and the weight of the electrode sheets 12 (W), is subtracted from the volume (V) of all films.

$$V_0 = V - (W/\rho)$$

[0025] The porosity and maximum pore diameter of the electrode sheet 12 can be adjusted according to the type of activated carbon used as the material constituting the electrode sheet 12, the amount of binder used, the roller pressure during electrode sheet formation, and other factors.

[0026] The conductive adhesive constituting the conductive adhesive layer 13 is composed of conductive carbon and a binder. The use of a conductive adhesive liquid dispersed in a dispersant enables the conductive adhesive layer 13 to penetrate the holes 12a of the electrode sheet 12, and an improvement in the joining strength between the collector 11 and the electrode sheet 12 can be realized after the dispersant is removed, due to the anchoring effect. In addition, the conductive adhesive layer 13 fills in the voids (air regions) present at the contact interface with the collector 11 due to the irregularities on the surface portion of the electrode sheet 12, resulting in a decrease in the volume of the airspaces present within the contact interface, and making it possible to prevent the internal resistance of the polarizable electrode body 10 from decreasing.

[0027] Examples of the conductive carbon used in the conductive adhesive include graphite, which shows high electrical conductivity due to the presence of delocalized π electrons; carbon blacks, which are spherical aggregates in which turbostratic structures are formed from numerous layers of graphite-type carbon microcrystals; and pyrolytic graphite, wherein methane, propane, acetylene, or another hydrocarbon is pyrolyzed in a gas phase and allowed to settle in the state of a thin film on a black plate used as a substrate. Graphite and carbon black are preferably used among these. Acetylene black is preferably used as a carbon black because it is highly structured and has excellent electrical conductivity.

[0028] The average particle diameter of such conductive carbon is preferably 0.5 to 50 μm . If the average particle diameter is greater than 50 μm , most of the granules will not be able to penetrate into the hole regions 12a of the electrode sheet 12; therefore, not only is it impossible to expect the joining pressure to increase as a result of the anchoring effect, but the degree of penetration required to yield a decrease in internal resistance will be difficult to achieve. If the average particle diameter is less than 0.5 μm , most of the granules will penetrate deep within the

holes 12a of the electrode sheet 12; accordingly, the conductive carbon is less likely to remain in the interface between the collector 11 and the electrode sheet 12, and no improvement in the joining strength can be realized. In addition, if the conductive carbon penetrates deep within the electrode sheet 12, the fine pores in the activated carbon constituting the electrode sheet 12 will be covered thereby, which will reduce the specific area of the activated carbon; i.e., the activity of the activated carbon will decline and the performance of the capacitor will inevitably deteriorate.

[0029] Examples of binders used in the conductive adhesive include water glass; sodium or ammonium salts of carboxymethyl cellulose or other cellulose derivatives; and polyvinyl alcohol, polyvinyl butyral, polyvinyl acetate, polybis(polybutene), or other thermoplastic resins.

[0030] The degree to which the conductive adhesive layer 13 composed of the conductive adhesive having the above structure penetrates into the hole regions 12a of the electrode sheet 12 is, with respect to the thickness of the electrode sheet 12, 0.15% or greater, and preferably 0.25% or greater, while also 30% or less, and preferably 15% or less. If the conductive adhesive layer is only able to penetrate to a depth that is less than 0.15% of the thickness of the electrode sheet 12, an improvement in joining strength due to the anchoring effect will not be obtained, and, depending on the circumstances, a layer of air will remain in the region between the electrode sheet 12 and the conductive adhesive layer 13, causing an increase in internal resistance. Conversely, if the conductive adhesive layer penetrates to a depth exceeding 30% of the thickness of the electrode sheet 12, the joining strength will improve, but the ratio of fine pores in the activated carbon constituting the electrode sheet that are covered over by the conductive adhesive will become excessively high, and the specific surface area of the activated carbon will decrease; by extension, the activity of the activated carbon will also decrease, inevitably resulting in a decline in electrostatic capacity.

[0031] The degree of penetration (expressed as a percentage) as denoted in the present specification refers to the ratio ($t/T \times 100$) where, after having used a cutter to cut the polarizable electrode body 10 in the thickness direction at an arbitrary point and observed the resulting cross-section under an electron microscope, t is the average distance between the distal portion of the side of the conductive adhesive layer 13 facing the electrode sheet 12 and the distal portion of the side of the electrode sheet 12 facing the conductive adhesive layer 13, and T is the average thickness of the electrode sheet 12. The degree to which the conductive adhesive layer

13 penetrates into the hole regions 12a of the electrode sheet 12 can be adjusted in accordance with the maximum pore diameter of the electrode sheet 12, the amount of conductive adhesive used, the pressure applied when the electrode sheet 12 and the collector 11 are laminated, and other factors.

[0032] The collector 11 is preferably composed of aluminum, stainless steel, titanium, tantalum, or another metal. The metals may be used in the form of a foil, plate, or sheet. The collector in the polarizable electrode of the present invention may be a smooth-surfaced metallic foil, metallic plate, metallic sheet, or the like. As shown in FIG. 1, the contact made in arbitrary locations between the collector 11 and the electrode sheet 12 enables the presence of the air layer to be reduced where the conductive adhesive 13 fills the voids present in the interface, while the anchoring effect resulting from the conductive adhesive 13 having penetrated into the holes 12a of the electrode sheet 12 allows the joining strength to be improved.

[0033] Metallic foils, thin metallic plates, and metallic sheets whose surfaces have been roughened so that irregularities are present thereon are more preferably used as the collector 11. Examples of roughening methods include sandblasting and etching; however, methods in which a chemical agent is used to chemically etch the material are particularly preferable because the fine pores and irregular state thereby formed on the surface of the collector are conducive to the anchoring effect of the adhesive.

[0034] FIG. 2 shows a polarizable electrode having a collector whose surface region has been roughened so that irregularities are present thereon. In this polarizable electrode body 10', some of the conductive adhesive constituting the conductive adhesive layer 13 has penetrated into the holes 12a of the electrode sheet 12, as well as into concavities 11'a of a collector 11', which allows the joining strength between both components to be improved. In such instances, the conductive adhesive that has penetrated into the concavities 11'a eliminates the air present in the concavities and prevents increases in the electric resistance due to the presence of the electrolyte when used in a capacitor, while also contributing to an improvement in the joining strength between the collector 11', the conductive adhesive layer 13, and the electrode sheet 12.

[0035] When using a collector 11' whose surface has been roughened so that irregularities are present thereon, a polarizable electrode body 10" having the structure shown in FIG. 3 can be obtained, depending on the amount of conductive adhesive and the pressure applied during lamination. In other words, the conductive adhesive layer 13 is interposed between the

collector 11' and the electrode sheet 12; however, on a microscopic level, convexities 11'b of the collector 11' are in contact with the convexities of the electrode sheet 12 over the entire polarizable electrode body 10". Further reductions in internal resistance can be realized in such instances. More specifically, two types of conductive paths can be formed; i.e., a conducting path from the collector 11' to the electrode sheet 12 via the conductive adhesive layer 13 (indicated by arrow A in FIG. 3) and a conductive path from the collector 11' directly to the electrode sheet 12 (indicated by arrow B in FIG. 3). Path B offers lower electric resistance than path A; therefore, the fact that two types of paths A and B are formed enables the resulting electric double-layer capacitor to have a high output as well as lower internal resistance.

[0036] A polarizable electrode body having the above-described structure can be manufactured according to the following method.

[0037] First, a conductive adhesive liquid composed of a conductive adhesive dispersed in a dispersant is prepared. The conductive adhesive liquid is preferably prepared using water, a lower alcohol, or the like as the dispersant, with a 20 to 30 wt% concentration of conductive carbon. Specifically, a conductive adhesive liquid having a composition as shown in Table 1 is preferably used. A suitable composition is preferably selected from Table 1 and used at a concentration of 1 to 30 times.

[0038]

[Table 1]

	Conductive carbon (average particle diameter)	Binder	Dispersant	Other
1	Natural graphite (3 μ m) 20-30 wt%	Carboxymethyl cellulose Na salt 4-16 wt%	Water 50-75 wt%	Ammonia several wt%
2	Natural graphite (3 μ m) 25-30 wt%	Methyl cellulose 5-20 wt%	Isopropyl alcohol 45-75 wt%	
3	Natural graphite (3 μ m) 25-30 wt%	Polyvinyl alcohol 5-20 wt%	Isopropyl alcohol 45-75 wt%	
4	Natural graphite (3 μ m) 25-30 wt%	Polyvinyl butyral 5-20 wt%	Isopropyl alcohol 45-75 wt%	
5	Natural graphite (3 μ m) 25-30 wt%	Polyvinyl acetal 5-20 wt%	Isopropyl alcohol 45-75 wt%	
6	Natural graphite (3 μ m) 25-30 wt%	Polybis polybutene 5-20 wt%	Isopropyl alcohol 45-75 wt%	
7	Natural graphite (3 μ m) 20-30 wt%	Acrylic acid resin-styrene copolymer 2-8 wt%	Water 50-75 wt%	Ammonia several wt%

	Conductive carbon (average particle diameter)	Binder	Dispersant	Other
8	Natural graphite (3 μm) 25-30 wt%	Water glass 5-20 wt%	Water 45-75 wt%	
9	Natural graphite (60 μm) 20-30 wt%	Carboxymethyl cellulose Na salt 4-16 wt%	Water 50-75 wt%	Ammonia several wt%
10	Acetylene black (40 μm) 20-30 wt%	Carboxymethyl cellulose Na salt 4-16 wt%	Water 50-75 wt%	Ammonia several wt%

[0039] The conductive adhesive liquid thus prepared is applied to at least one surface of the electrode sheet and the collector. The liquid may be applied on the bonding surface of either the electrode sheet or the collector, or to both. However, a preferable method involves the conductive adhesive liquid being applied to the bonding surface of the collector. The surface of the electrode sheet is actually an aggregate of particles, with irregularities present along the entire surface thereof; accordingly, when the abovementioned conductive adhesive liquid is applied to the electrode sheet side, the conductive adhesive liquid will permeate the holes of the electrode sheet, and the proportion to which the conductive adhesive penetrates the holes will inevitably surpass the suitable degree of penetration at which the joining strength will improve and the internal resistance will decrease. Even if mass production is taken into account, the conductive adhesive liquid is preferably applied to the collector, which is stronger than the electrode sheet.

[0040] The conductive adhesive liquid is preferably applied in an amount of approximately 2 to 15 g/m^2 , and more preferably approximately 3 to 10 g/m^2 , expressed in terms of the amount of conductive adhesive (i.e., the combined amount of conductive carbon and binder). The amount will depend on the magnitude of pressure applied during lamination in the subsequent step, but a larger amount will usually result in an increase in the thickness of the resulting conductive adhesive layer; therefore, if a surface-roughened metallic foil or the like is used as the collector, a polarizable electrode body of the type shown in FIG. 2 will be obtained.

[0041] Next, a laminated article is formed by layering the polarizable electrode material sheet and the collector with the conductive adhesive liquid coating interposed therebetween. Various lamination methods can be considered; the sheet and collector may merely be layered, but are preferably passed between rolls or otherwise compressed so that the lamination interfaces will be securely bound together. If a surface-roughened metallic foil is used as the collector, a

polarizable electrode body in which the convexities of the collector and the convexities of the metallic sheet are in contact, as shown in FIG. 3, can be obtained by appropriately controlling the amount of conductive adhesive applied and the lamination pressure,.

[0042] The dispersant is then removed from the conductive adhesive layer of the resulting laminated article. A variety of methods may be considered for use in removing the dispersant, but a method involving hot-blast drying is preferably employed. A temperature near the boiling point of the dispersant should be chosen for the hot blast temperature. Removing the dispersant via drying or another method will leave the binder and the conductive adhesive composed of conductive carbon, thereby serving to bond the collector and the electrode sheet together.

[0043] A polarizable electrode body (FIGS. 1 through 3) is thus produced in which an electrode sheet is laminated onto and integrated with the surfaces of both sides of a collector with a conductive adhesive interposed therebetween. It must be noted that only one side of the collector is depicted in FIGS. 2 and 3.

[0044] The joining strength between the collector and the electrode sheet is high in a polarizable electrode body having a structure such as has been described above. It is thus possible to fabricate a long polarizable electrode body that can be wound up, stored/transported in the form of a roll or otherwise handled. The polarizable electrode accordingly has exceptional properties as relates to its manufacture, storage and transport, and durability. The polarizable electrode body also has a lower internal resistance because the amount of air present between the collector and the electrode sheet is made lower than in conventional practice.

[0045] In the electric double layer capacitor of the present invention, assemblies obtained by arranging the polarizable electrode body 10 as shown in FIG. 1 and a separator 15 in an alternating fashion (see FIG. 4) are provided in proximity in a row arrangement, and the regions between the polarizable electrode 10 and the separator 15 are filled with an electrolyte. Separators conventionally used in electric double-layer capacitors can be used as the separator 15. Specific examples include hydrophilized porous sheets made from polytetrafluoroethylene, polyethylene, polypropylene, or another similar material; and porous sheets obtained from sisal fibers.

[0046] In FIG. 4, the symbol 9 refers to a collecting terminal attached to the collector. A collecting lead is attached to the collecting terminal 9. It must be noted that the electric double-layer capacitor element shown in FIG. 4 is an example in which the polarizable electrode 10 is

used, but the same structure may also be obtained when using the polarizable electrode 10' or 10". In addition, the plurality of polarizable electrode bodies that are provided in proximity in a row arrangement may all be of the same type, or the arrangement may consist of differing types of polarizable electrode bodies.

[0047] Furthermore, as shown in FIG. 5, the polarizable electrode bodies provided to the outermost ends of the plurality of electrode bodies provided in proximity in a row arrangement may be polarizable electrode bodies in which an electrode sheet has been laminated on only one surface of the collector.

[0048] The polarizable electrode body of the present invention, which has a low internal resistance, is used in the electric double-layer capacitor of the present invention. The capacitor is thus able to be made compact, while exhibiting a high electric capacity and output density.

[0049]

[Working Examples] The present invention will subsequently be described in further detail through working examples.

[0050] Working Example 1: Ethanol was added to a mixture consisting of 85 wt% activated carbon powder (specific surface area: 2200 m²/g; average particle diameter: 7 μm), 7 wt% Ketjen black, and 8 wt% polytetrafluoroethylene. The resulting mixture was kneaded and rolled between rolls to yield a long electrode sheet having a width of 10 cm, a thickness of 0.8 mm, a porosity of 66%, and a maximum pore diameter of 18 μm. High-purity aluminum foil having a thickness of 50 μm and a width of 15 cm was used as the collector. The conductive adhesive was produced by preparing a conductive adhesive liquid, which was obtained by dispersing natural graphite for use as the conductive carbon (average particle diameter: 3 μm), and carboxymethyl cellulose Na salt as a binder, in a dispersant; and using the liquid in the manufacturing process. The composition of the resulting conductive adhesive liquid is 30 wt% conductive carbon, 8 wt% binder, 60 wt% water, and 2 wt% ammonia.

[0051] The conductive adhesive liquid was applied with coating rolls to both surfaces of the collector so that 4 cm or more was left in the width direction at one end of the collector. The conductive adhesive was applied in an amount of 20 g/m² (i.e., 7 g/m² when expressed in terms of the amount of conductive adhesive corresponding to the combined amount of the conductive carbon and binder used). After the liquid had been applied, the long electrode sheet was laid on

the coated portion of the collector (on both surfaces thereof), and the resulting assembly was passed through compression rolls to yield a laminated sheet in which the contact interfaces were securely bonded together. The resulting laminated sheet was passed through a continuous hot-blast dryer set at a temperature of 110°C, so that the dispersant was removed from the conductive adhesive layer, resulting in a long polarizable electrode body. It should be noted that the rate at which the assembly was passed through the dryer was such that the residence time therein was 3 min.

[0052] The resulting polarizable electrode body in the form of a long sheet was stamped into squares measuring 10 cm per side, and collecting terminals measuring 2 cm × 4 cm were attached to the collector portions of the polarizable electrode bodies. Next, an assembly consisting of polarizable electrode bodies and separators was fabricated as shown in FIG. 4, and a total of 13 of these assemblies were arranged in parallel to form a single unit, as shown in FIG. 6. The unit was vacuum-dried in this state at a temperature of 200°C for 3 hours, and then housed in an aluminum case 20. Collecting leads 23 were then attached to the collecting terminals, and positive and negative terminals were attached to the collecting leads. A propylene carbonate solution of tetraethylammonium tetrafluoroborate having a concentration of one mole was injected as an electrolyte 22, and a cover 21 was attached to seal the case 20, resulting in a square-shaped electric double-layer capacitor.

[0053] In addition, the 10 × 10 cm square polarizable electrode body that had been prepared in advance was cut along the thickness direction in an arbitrary location, and the resulting cross-sectional surface was examined under a microscope to determine the degree to which the conductive adhesive had penetrated.

[0054] Working Example 2: The procedure of Working Example 1 was followed to produce a square-shaped electric double-layer capacitor and determine the degree to which the conductive adhesive penetrated, except that the composition of the conductive adhesive liquid was changed to 30 wt% acetylene black (average particle diameter: 40 µm), 8 wt% carboxymethyl cellulose Na salt, 60 wt% water, and 2 wt% ammonia.

[0055] Working Examples 3 and 4: The procedure of Working Example 1 was followed to produce square-shaped electric double-layer capacitors and determine the degree to which the conductive adhesive penetrated, except that a rough-etched aluminum foil was used as the collector (Working Example 3), and a rough-etched aluminum foil was used as the collector and

the converted amount of conductive adhesive applied was changed to 3.5 g/m² (Working Example 4).

[0056] Comparative Example 1: A square-shaped electric double-layer capacitor was produced in the same manner as performed in Working Example 1, except that the composition of the conductive adhesive liquid was changed to 30 wt% natural graphite (particle diameter: 80 μ m), 8 wt% carboxymethyl cellulose Na salt, 60 wt% water, and 2 wt% ammonia.

[0057] The resulting polarizable electrode was cut along the thickness direction in an arbitrary location and the resulting cross-section was examined under a microscope, which showed that the conductive carbon (natural graphite) had a large particle diameter, and thus could not penetrate into the holes of the electrode sheet.

[0058] Comparative Example 2: The procedure of Working Example 1 was followed to produce a square-shaped electric double-layer capacitor and determine the degree to which the conductive adhesive penetrated, except that an electrode sheet with a width of 10 cm, a thickness of 0.8 mm, a porosity of 66%, and a maximum pore diameter of 30 μ m was used.

[0059] Comparative Example 3: A square-shaped electric double-layer capacitor was produced in the same manner as performed in Working Example 1, except that a surface-roughened high-purity aluminum foil was used as the collector; electrode sheets were directly laminated on either side thereof without a conductive adhesive interposed therebetween; and the assembly was rolled using rolls to yield a laminated sheet.

[0060] Comparative Example 4: A square electric double-layer capacitor was produced in the same manner as performed in Working Example 1, except that a high-purity aluminum expanded metal having an SW (short width) of 1.0 mm, an LW (long width) of 2.0 mm, an St (strand width) of 0.23 mm, and a t (original thickness) of 80 μ m was used as the collector; electrode sheets were directly laminated on either side thereof without a conductive adhesive interposed therebetween; and the assembly was rolled using rolls to yield a laminated sheet.

[0061] Measurements were made of the electrostatic capacity and internal resistance of the electric double-layer capacitors obtained in Working Examples 1 through 4 and Comparative Examples 1 through 4. The results are shown in Table 2.

[0062]

[Table 2]

No.	Collector	Electrode sheet	Conductive adhesive		Degree of penetration (%)	Characteristics				
			Material	Max. pore diam. (μm)		Conductive carbon particle diameter (μm)	Amt. applied (g/m ²)	Internal resistance (mΩ)	Electrostatic capacity (F)	Volume (cc)
Working Examples	1	Aluminum foil	18	7	7	1.0	16	4300	460	9.3
	2	Aluminum foil	18	40	7	0.8	16	4300	460	9.3
	3	Etched aluminum foil	18	7	7	1.0	15	4300	460	9.3
	4	Etched aluminum foil	18	7	3.5	1.0	14	4300	460	9.3
Comparative Examples	1	Aluminum foil	18	80	7	No penetration	19	4300	460	9.3
	2	Aluminum foil	30	7	7	31.3	19	4210	460	9.2
	3	Roughened aluminum foil	18	—	—	—	19	4300	460	9.3
	4	Expanded aluminum metal foil	18	—	—	—	23	4300	460	9.3

[0063] As can be understood from Table 2, the electric double-layer capacitors in which the polarizable electrode of the present invention is used, wherein the degree to which the conductive adhesive penetrates lies within a prescribed range, have a lower internal resistance than the electric double-layer capacitors of the comparative examples. The internal resistance particularly decreased in Working Example 4, which had a roughened surface and less of the conductive adhesive. This was due to the formation of a conductive adhesive layer thin enough so that the convexities of the collector and the convexities of the electrode sheet came into direct contact with each other.

[0064] By contrast, the internal resistance increased in the electric double-layer capacitors containing polarizable electrode bodies in which no conductive adhesive layer was present

(Comparative Examples 3 and 4), in which the conductive adhesive did not penetrate into the holes in the electrode sheet (Comparative Example 1), and in which the degree to which the conductive adhesive penetrated was excessive, with little of the adhesive believed to have remained at the interface between the collector and the electrode sheet (Comparative Example 2). All of these results are believed to be due to an increase in the liquid-phase space present in the contact interface between the collector and the electrode sheet. It is also thought that the electrostatic capacity declined in Comparative Example 2 because the conductive adhesive penetrated deep into the holes of the electrode sheet, and thus many of the fine pores of the activated carbon constituting the electrode sheet were covered thereby.

[0065]

[Effect of the Invention] The polarizable electrode body of the present invention has exceptional joining strength between the collector and the electrode sheet, thus enabling fabrication in long sheets and providing exceptional characteristics related to its suitability for mass-production, storage, and transport. In addition, little air needs to be present in the contact interface between the collector and the electrode sheet, which results in lower internal resistance.

[0066] Accordingly, an electric double-layer capacitor in which the polarizable electrode body of the present invention is used will have exceptional productivity and compactness of size, while exhibiting a high electric capacity and high output density.

[Brief Description of the Drawings]

[Figure 1] Schematic view showing the structure of the polarizable electrode body of the present invention.

[Figure 2] Schematic view showing the structure of one side of the polarizable electrode body as defined in Claim 4.

[Figure 3] Schematic view showing the structure of one side of the polarizable electrode body as defined in Claim 5.

[Figure 4] Diagram showing the structure of an assembly formed from a separator and the polarizable electrode body of the present invention.

[Figure 5] Diagram showing the appearance of a plurality of electric double-layer capacitor elements provided in proximity in a row arrangement.

[Figure 6] Schematic view showing the structure of the electric double-layer capacitor of one working example of the present invention.

[Figure 7] Schematic diagram showing the structure of a conventional polarizable electrode body.

[Key]

10, 10': Polarizable electrode body

11, 11': Collector

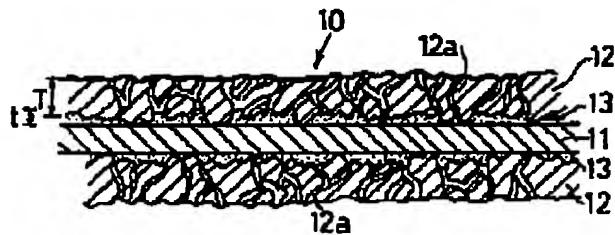
12: Electrode sheet

12a: Hole

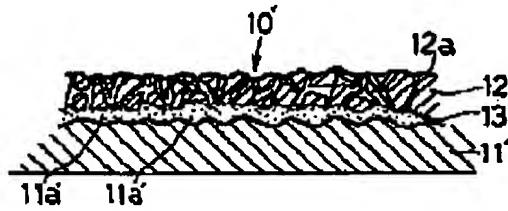
13: Conductive adhesive layer

15: Separator

[Figure 1]

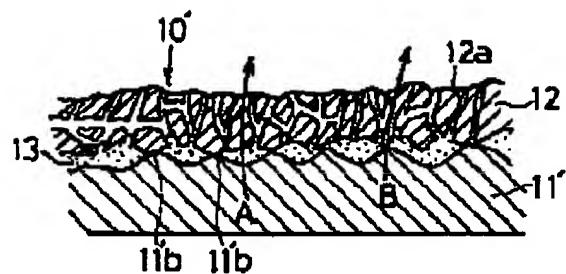


[Figure 2]

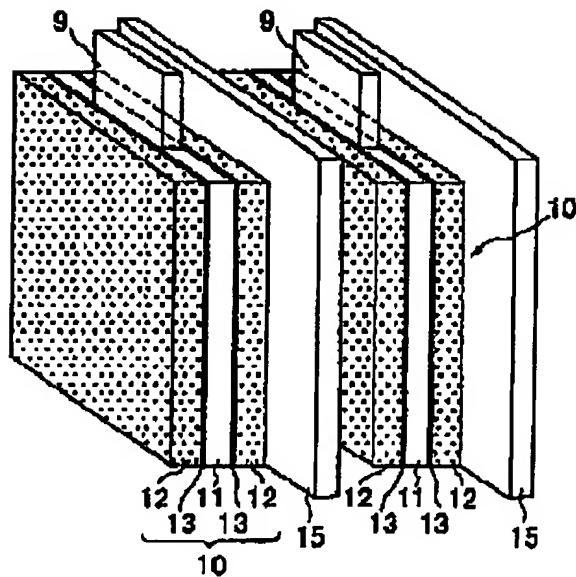


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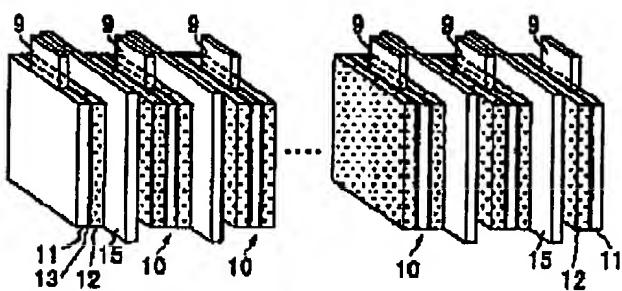
[Figure 3]



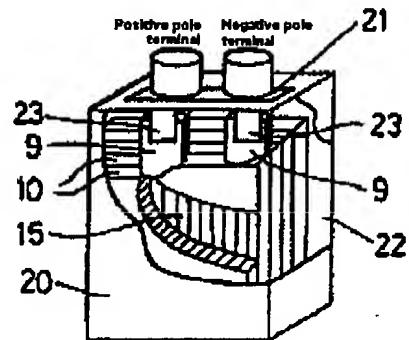
[Figure 4]



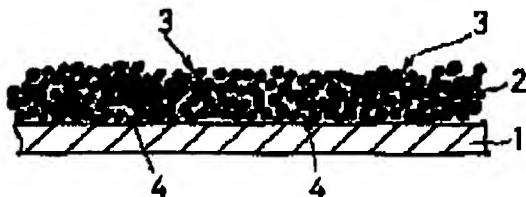
[Figure 5]



[Figure 6]



[Figure 7]



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